Implications and remediations of DMAEA-Q type polymer hydrolysis in wastewater treatment plants

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ABSTRACT

The present paper outlines the impact of hydrolysis occurring in DMAEA-Q type polymers in the dewatering facilities of municipal wastewater treatment plants. Laboratory studies of polymer hydrolysis kinetics were combined with full-scale dewatering experiments to investigate the influence of polymer charge loss on polymer consumption and cake dry matter yields. The results indicate that prolonged polymer storage leads to important charge loss effects, resulting in increased dosage requirements for satisfactory dewatering performance. Fortunately, charge loss effects due to hydrolysis upon polymer storage could be minimized by acidifying the polymer batches. Furthermore, cake dry matter contents obtained from dewatering tests with freshly prepared polymer batches suggested that acidification of the polymer batch also had a beneficial effect on the conditioning efficiency of the polymer solution. The results from this study thus stress the influence of pH on the shelf life and efficiency of polymer solutions in wastewater treatment plants. As a consequence, polymer preparation and storage procedures should be adapted to the polymer consumption pattern and pH of the medium used for polymer batch production.

Key words | cationic polyelectrolytes, dewatering, dry matter content, polymer dosing

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INTRODUCTION

Cationic polymers, also denoted as polyelectrolytes, enjoy an increasing popularity in various applications and especially in sludge treatment, where they are applied in thickening and dewatering processes. Being produced as copolymers of uncharged and cationic monomers, a large variety of polyelectrolytes is available on the market, differing in chemical composition, molecular weight, degree of cross-linking and cationic charge density. The synthetic polyelectrolyte that makes up the vast majority of the market for municipal wastewater treatment, about 75%, is a copolymer of acrylamide and quaternised dimethylaminoethylacrylate (DMAEA-Q).

DMAEA-Q type polymer hydrolysis

In order to reduce the ecotoxicological impact of DMAEA-Q type polymers when released to the environment,

they are designed to quickly release their cationic side groups by basic hydrolysis at the ester bond (Figure 1).

This hydrolysis phenomenon is clearly promoted by basic pH values, but is also stimulated by high conductivity and high temperature (Aksberg & Wagberg 1989; Lafuma & Durand 1989).

A previous study (Saveyn *et al.* 2008) has shown that in dilute solutions, this hydrolysis process occurs fast and even at neutral to slightly acidic pH values. This can be explained by the colloidal nature of these polymers, which often have a very high molecular weight and therefore exhibit a particulate behavior (Dickinson & Eriksson 1991). The concentration of the negatively charged hydroxyl ions near the polymer surface is expected to be much higher than in the bulk solution, in order to compensate for the positive polymer charges. Consequently, the positively
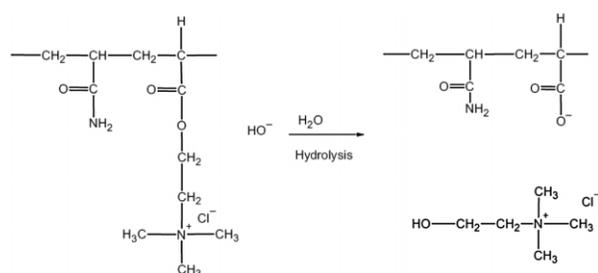
Figure 1 | Hydrolysis reaction of quaternised dimethylaminoethyl acrylate (DMAEA-Q) copolymers (Saveyn *et al.* 2008).

charged protons exhibit a lower concentration near the polymer surface than in the bulk, and therefore the pH close to the polymer surface may be much higher than the bulk solution pH.

Taking into account these literature findings, the widely used practice of polymer solution preparation in non-buffered media such as effluent or tap water, suggested that polymer may be at risk of hydrolyzing swiftly in many treatment plants. The current paper therefore focuses on the hydrolysis effects occurring in the polymer make-up installations of a series of wastewater treatment plants (WWTPs). The rationale behind this study is that hydrolysis effects might also affect the flocculation and dewatering processes in a way that is undesired. It will be assessed whether hydrolysis effects have a sizable impact on the dewatering performance and how the possible adverse effects can be remediated.

METHODS

In a first stage, a survey was organised at 25 WWTPs to investigate sludge production, polymer concentration and dosage, polymer type and dewatering equipment. From this list, six WWTP's were selected, characterized by a large sludge production and sufficient regional spreading over the region of Flanders (A, D, G, H, L and O). To this selection, four WWTP's were added for varying reasons: B (high iron content in effluent), L2 (other polymer manufacturer) and R and W (high susceptibility to polymer hydrolysis due to high effluent pH and conductivity). From these ten plants, effluent and concentrated polymer samples were collected.

For the laboratory tests, polymer solutions were made at the same concentration of active polymer as in the corresponding plants. These solutions were made in original effluent, 2 mM acetate buffer in distilled water (pH 4.5) and acidified effluent (pH 4.5 by addition of HCl). The charge density of the different polymer solutions was then followed over time by charge titration (Charge Analyzer II, Rank Brothers, UK). All experiments were performed at ambient temperature (21 ± 1°C).

Following laboratory measurements, two wastewater treatment plants (R, B) were selected for full scale studies. Here, the effect of acid addition during polymer solution make-up was studied both for the effect on prolonged storage of the polymer solution and its immediate impact on the dewatering operation. WWTP R was equipped with one single centrifuge (Alfa Laval NX 4800) and was used to investigate long term storage. WWTP B was equipped with two identical centrifuges (Alfa Laval NX 4850) as well as two polymer make-up units and thus best suited to run parallel tests to assess the immediate impact of polymer hydrolysis. In WWTP R, polymer batches were made and stored in $1 \, m^3$ cubitainers. This was done in two ways: either the regular make-up program was followed or concentrated HCl (30%, VWR) was dosed continuously during polymer make-up in order to keep the pH value around 4.5. After three days–to simulate storage over a time period of a weekend–these polymer batches were used for conditioning sludge prior to dewatering. In WWTP B, polymer batches were made in the two polymer make-up units and sludge was fed to the two centrifuges. The two centrifuges were operated at the same feeding rate at any time during the experiment. After adjustment of the polymer feeding rate, a delay of at least 30 minutes was respected prior to sampling sludge cake, in order to avoid transition phenomena.

RESULTS AND DISCUSSION

The results obtained for the laboratory tests and full-scale trials will be discussed separately in the following sections.

Laboratory-scale tests

Table 1 shows the pH and conductivity values for the effluent samples taken from the 10 wastewater treatment

Table 1 | Overview of different WWTP parameters

| Plant name	Effluent pH	Effluent conductivity (μS/cm)	Polymer concentration (% active) & dewatering equipment	
A	7.0	1,186	0.32	Belt press
B	7.3	611	0.30	Centrifuge
D	6.9	657	0.13	Thickener
			0.39	Centrifuge
G	7.2	683	0.15	Thickener
			0.42	Centrifuge
H	7.0	1,350	0.18	Thickener
			0.27	Filter press
L	7.3	725	0.23	Centrifuge
L2	7.0	572	0.23	Filter press
O	7.1	2,170	0.20	Filter press
R	7.7	1,210	0.30	Centrifuge
W	7.1	750	0.25	Filter press

plants. It is seen that the pH is situated around neutral to slightly basic values. Especially plant R shows a high pH value, which was thought to be due to intake of a considerable fraction of industrial influent. Furthermore, some WWTPs exhibit high conductivity in the effluent, often due to either intake of industrial influent or the proximity of the sea.

Table 1 also displays the polymer concentrations in percentage active polymer. Except for bead formulations, most polymer products have less than 100% activity, yet it is
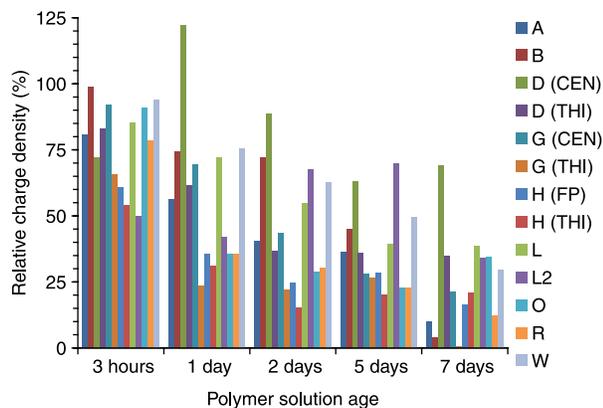
Figure 2 | Relative charge density as function of time for polymers prepared in effluent (reference value 100% = maximum value obtained in acetate buffer solution) (CEN = centrifuge, THI = thickener, FP = filter press). Subscribers to the online version of *Water Science and Technology* can access the colour version of this figure from http://www.iwaponline.com/wst
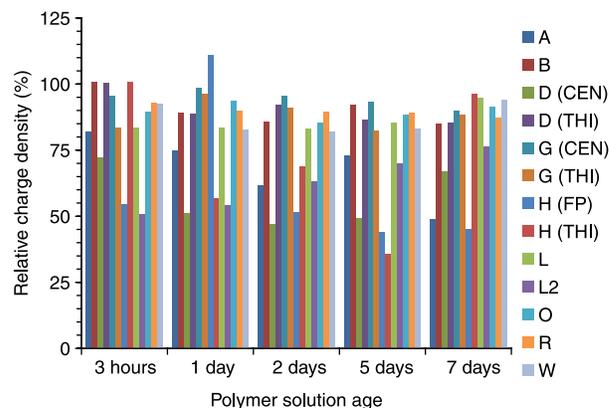
Figure 3 | Relative charge density as function of time for polymers prepared in acidified effluent (reference value 100% = maximum value obtained in acetate buffer solution) (CEN = centrifuge, THI = thickener, FP = filter press). Subscribers to the online version of *Water Science and Technology* can access the colour version of this figure from http://www.iwaponline.com/wst

the concentration of active polymer in the polymer solution that determines it flocculating efficiency and probably its hydrolysis kinetics. Some plants have two polymer dosing systems, one for the mechanical belt thickener and one for the dewatering device. In this case, the plants were equipped with an anaerobic digester and the thickener served to concentrate the sludge going to the digester.

Based on the values displayed in Table 1 for pH and polymer concentration, it may be estimated that some plants are at risk of pronounced polymer hydrolysis. Indeed, Saveyn *et al.* (2008) discussed that hydrolysis effects become more pronounced when either the pH increases or the polymer concentration in solution decreases.
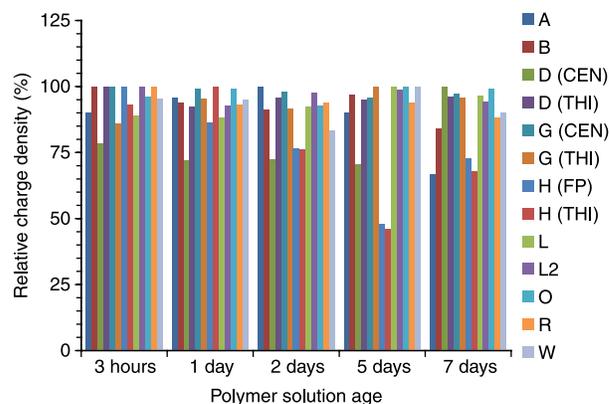
Figure 4 | Relative charge density as function of time for polymers prepared in acetate buffer (reference value 100% = maximum value obtained in acetate buffer solution) (CEN = centrifuge, THI = thickener, FP = filter press). Subscribers to the online version of *Water Science and Technology* can access the colour version of this figure from http://www.iwaponline.com/wst

Figures 2, 3 and 4 represent the measured charge density of the polymer solutions as a function of time in effluent, acidified effluent and acetate buffer, respectively. The index 100 stands for the highest polymer charge density measured in the acetate buffer.

The charge density evolution in the original effluent clearly demonstrates the impact of polymer hydrolysis on charge loss. Three hours after polymer make-up, some polymers have already lost more than half of their maximal charge density. After one day, 6 out of 13 polymers have lost more than half of their potential charge density. After one week, only one polymer has retained more than 50% of its theoretical charge density.

In the acidified effluent, the picture looks clearly different. At the beginning of the kinetic experiment, some polymer samples exhibit a charge density inferior to the one in buffer. Yet, there appears to be little loss of charge in the course of time for the majority of the samples. The lower charge density in the beginning of the experiment may be explained by the presence of suspended material that immediately interacts with the polymer and hence reduces the available charge. This hypothesis is confirmed when comparing the values of the charge densities at 3 hours after make-up in the regular effluent (Figure 2) and acidified effluent (Figure 3) by a paired T-test. The latter states that the values of charge density at 3 hours in the two kinds of systems are not significantly different at the 95% level. However, in the acidified effluent system, the acid pH clearly slows down the charge loss by hydrolysis, as can be seen in Figure 3.

For the polymer samples prepared in the buffer medium, most polymers remain stable for several days and even after a week, 8 out of 13 samples still retain more than 90% of their maximum charge density (Figure 4). It was shown earlier by Saveyn *et al.* (2008) that preparation of polymer in buffered medium is necessary in order to be able to perform reliable charge titration measurements.

No clear correlations could be found between pH or conductivity and charge loss in the polymer solutions based on regular effluent. Only a statistically significant (95% level) positive correlation was found between the remaining charge after one day and the polymer concentration in the solution, thus indicating the importance of polymer dilution on the susceptibility to hydrolysis effects. Given the complex nature of effluent, the interplay between the different parameters may have had an important effect on hydrolysis kinetics.

Full-scale tests on polymer storage

One of the WWTPs that suffers from a rapid charge decline is plant R. To investigate the impact of this charge decline on the necessary polymer dose for satisfactory dewatering, batches of acidified polymer and regular polymer solutions were tested after three days of storage. Prior to these tests, the immediate effect of acidification was tested as well.

The plant aims at obtaining dry matter contents of at least 30% for dewatered sludge. Therefore, polymer dosage is adjusted until this value is obtained. Local plant staff is very well acquainted with the dewatering operation and can rapidly assess whether the dewatered sludge meets the criteria, based on visual observations of the dewatered sludge lumps (size and stickiness) and centrate quality (color and turbidity). Yet, dry matter contents of the dewatered sludge are also determined analytically on a frequent base.

The first day of the field trials, a dosage of 7.6 kg active polymer/ton dry matter resulted in a cake dry matter content of 31.4 ± 0.6% (average ± standard deviation) in the case of acidified polymer and 30.6 ± 0.5% in case of regular polymer. Although not statistically significant, these data suggest some slight improvement of the sludge dewatering by the acidification of the polymer sample. Yet, the benefits of polymer batch acidification were most clearly noticed after prolonged polymer storage. Acidified polymer stored for 3 days only needed a dose of 8.2 kg active polymer/ton dry matter to reach a cake dry mater content of 31.0%. Although these tests were performed at a different moment in time than those with freshly prepared polymer solutions–hence making a direct dose comparison difficult–it is seen that the polymer requirements for the acidified polymer batches are only slightly higher than for the fresh polymer batches. However, for polymer prepared in non-acidified effluent, a dose of at least 12.0 kg active polymer/ton dry matter was needed to obtain a satisfactory dewatering result (31.4% dry mater), i.e. a 46% higher polymer dose than in the case of acidified polymer. The amount of concentrated HCl (concentration of 30%)

that needed to be dosed for sufficient acidification was on average 0.334 kg/kg active polymer. Comparing the cost of polymer, about 3 to 4 Euro per kg active polymer, to the cost of HCl (30%), 0.09 Euro per kg, it is seen that the additional chemical cost is less than 1% in most cases. Hence, the savings that can be made by acid addition in situations of potential efficiency loss, such as overnight or weekend storage, largely compensate for the chemical cost. This experiment also demonstrated that it should be an advisable practice to consume all prepared polymer batches within a few hours, and avoid storing large polymer quantities for prolonged time periods. Such a measure will also have additional benefits, such as reduction of odorous and toxic amine compounds formed by basic hydrolysis (Chang *et al.* 2005), and does not imply any investment or operational costs at all.

Full-scale tests on immediate effects of polymer acidification

Another plant that showed pronounced charge loss after one week storage of the polymer in the laboratory-scale trials, was plant B. Given that it holds two identical centrifuges and two polymer make-up units, this plant offered the possibility of running parallel dewatering tests with regular polymer batches and acidified polymer batches.

Tests were run in parallel, dosing polymer at the same rate on both centrifuges at every instant. The following day, the centrifuges were swapped and the same kind of parallel tests were performed. In this way, any possible effect of the centrifuges and the make-up unit could be assessed, apart from the effect of the polymer acidification.

Figure 5 shows the dry matter contents obtained for the different polymer doses. In this plant, a cake dry matter content of 24 to 25% was targeted.

The differences noted between CF1 and CF2 indicate that the dewatering devices have a large impact on the dewatering results, although they were supposed to be identical. Reasons for this may be mechanical aspects like wear or small differences in polymer make-up and distribution. Comparing the results obtained on each centrifuge, it is seen that the acidified polymer batches yield better results than the regular batches in five out of six cases. The average improvement is 1.32% with a 95% confidence
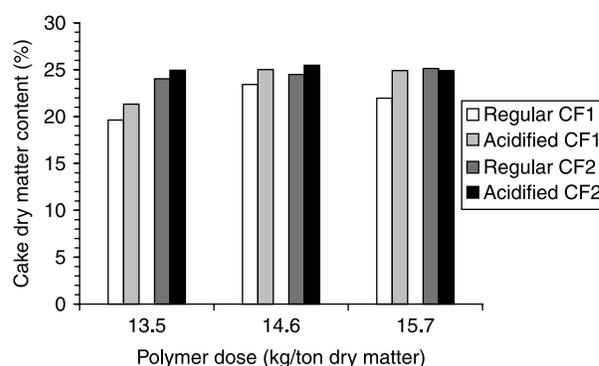

Figure 5 | Cake dry matter contents obtained for different polymer dosages during dewatering runs at plant B. Experiment performed with either regular or acidified polymer batches, on both centrifuges 1 and 2 (CF1 and CF2).

interval of [0.47% 2.16%], which excludes zero and thus indicates a significant improvement of the acidified batches, compared to the regular batches.

A clear explanation for the possible instantaneous effects of polymer acidification is not at hand. Figures 2 and 3 do not show a large difference in the polymer activity after 3 hours, with both values around 100% of their maximum level. However, in the kinetic laboratory tests, the charge densities were also measured at time 0 h, often resulting in a value which was much lower than charge density after 3 hours. This may be due to the well-known fact that polymer batches need some time to ripen, i.e. to unfold their chains. Therefore, these data have been omitted from Figures 2 to 4. In the case of plant B, it was seen that the charge density was only at 22.9% of its maximum value at time 0 h in regular effluent, whereas it was already at 76.8% of its maximum value at time 0 h in acidified effluent. This may suggest accelerated unfolding of the polymer chains in the acidified effluent, probably due to increased intra-molecular electrostatic repulsion, and therefore rapid availability of the charges for flocculation. Tonge & Tighe (2001) indeed reported varying unfolding behavior of charged polymers as a function of pH for many kinds of cationic polyelectrolytes.

At 15 kg of active polymer dosed per ton dry matter content, and again assuming an increase of 1% of the chemical cost due to acid addition, acidification costs about 0.53 Euro per ton dry matter. The gain here is realized in reducing the disposal costs. Recent data on disposal costs in the EU are given by Paul *et al.* (2006) and are on average 320 Euro/ton dry matter content for a cake at 20% dryness,

or 64 Euro/ton dewatered cake. Hence, an increase in dry matter content of 1.32%, e.g. from 24 to 25.32%, results in a reduction in disposal costs of 13.7 Euro per ton dry matter. Even an increase of 0.1% in dry matter, from 24.0 to 24.1%, would still yield a reduction in disposal costs of more than 1 Euro/ton dry matter, more than double the additional chemical cost. It is therefore clear that the realizable profit will be determined by the annual sludge production and the investment and maintenance costs of the acid dosing installation, rather than by the acid consumption.

CONCLUSIONS

Kinetic laboratory tests have shown that hydrolysis effects can cause a rapid charge decline in polymer solutions prepared in effluent, a common method of preparation in many wastewater treatment plants. An important factor related to this hydrolysis is the pH of the system, which is often too high to prevent basic hydrolysis. By experiments on full scale, it was shown that acidification of the effluent used for polymer solution preparation was very useful in preventing charge loss prevention due to prolonged storage. Therefore, it is advised to either consume all prepared polymer solutions rapidly or acidify them before prolonged storage.

In another plant, with two parallel dewatering installations, an investigation was made of the impact of the polymer batch acidification on the cake dry matter content upon immediate use of the polymer solution. The results from these experiments suggested an immediate improvement of the polymer efficiency by acidification as well. In practice, the usefulness of the acidification treatment will depend on the polymer consumption savings or cake dry matter content improvements versus the required investment costs and the annual sludge production. Yet the results from this study stress the influence of pH on the shelf life and efficiency of polymer solutions. Treatment plants characterized by infrequent polymer use or high pH values of the medium used for polymer preparation are therefore advised to pay the necessary attention to their polymer preparation and storage procedures.

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